

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
 US Department of Commerce  
 United States Patent and Trademark  
 Office, PCT  
 2011 South Clark Place Room  
 CP2/5C24  
 Arlington, VA 22202  
 ETATS-UNIS D'AMERIQUE  
 in its capacity as elected Office

Date of mailing (day/month/year) 31 May 2002 (31.05.02)	
International application No. PCT/US01/11806	Applicant's or agent's file reference PCT/98-21
International filing date (day/month/year) 10 April 2001 (10.04.01)	Priority date (day/month/year) 10 April 2000 (10.04.00)
Applicant HAMES, Bonnie, R.	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:  
02 November 2001 (02.11.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was  
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer ENGER Charlotte Telephone No.: (41-22) 338.83.38
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## PATENT COOPERATION TREATY

PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>PCT/98-21</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/US 01/ 11806</b>	International filing date (day/month/year) <b>10/04/2001</b>	(Earliest) Priority Date (day/month/year) <b>10/04/2000</b>
Applicant <b>MIDWEST RESEARCH INSTITUTE et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1

☐ None of the figures.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/11806

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F1/68 C02F1/58

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 595 489 A (SCOUTEN CHARLES G) 17 June 1986 (1986-06-17)	1, 2, 6
A	the whole document	3-5, 7, 8
X	EP 0 112 723 A (EXXON RESEARCH ENGINEERING CO) 4 July 1984 (1984-07-04)	1, 6
A	the whole document	2

☐

Further documents are listed in the continuation of box C.

☒

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

1 November 2001

Date of mailing of the international search report

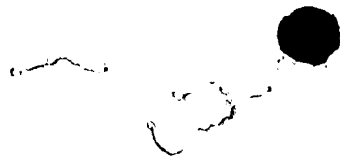
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Name and mailing address of the ISA

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/11806

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 4595489	A	17-06-1986	BR	8307122 A	07-08-1984
			EP	0112723 A2	04-07-1984
			JP	59130230 A	26-07-1984
			US	4661637 A	28-04-1987
			ZA	8309596 A	28-08-1985
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EP 0112723	A	04-07-1984	BR	8307122 A	07-08-1984
			EP	0112723 A2	04-07-1984
			JP	59130230 A	26-07-1984
			US	4595489 A	17-06-1986
			US	4661637 A	28-04-1987
			ZA	8309596 A	28-08-1985
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(43) International Publication Date  
18 October 2001 (18.10.2001)

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(10) International Publication Number  
**WO 01/77031 A2**

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[US/US]; 2522 West 104th Circle, Westminster, CO 80234 (US).

(21) International Application Number: PCT/US01/11806

(22) International Filing Date: 10 April 2001 (10.04.2001)

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(71) Applicant (for all designated States except US): MID-  
WEST RESEARCH INSTITUTE [US/US]; 425 Volker  
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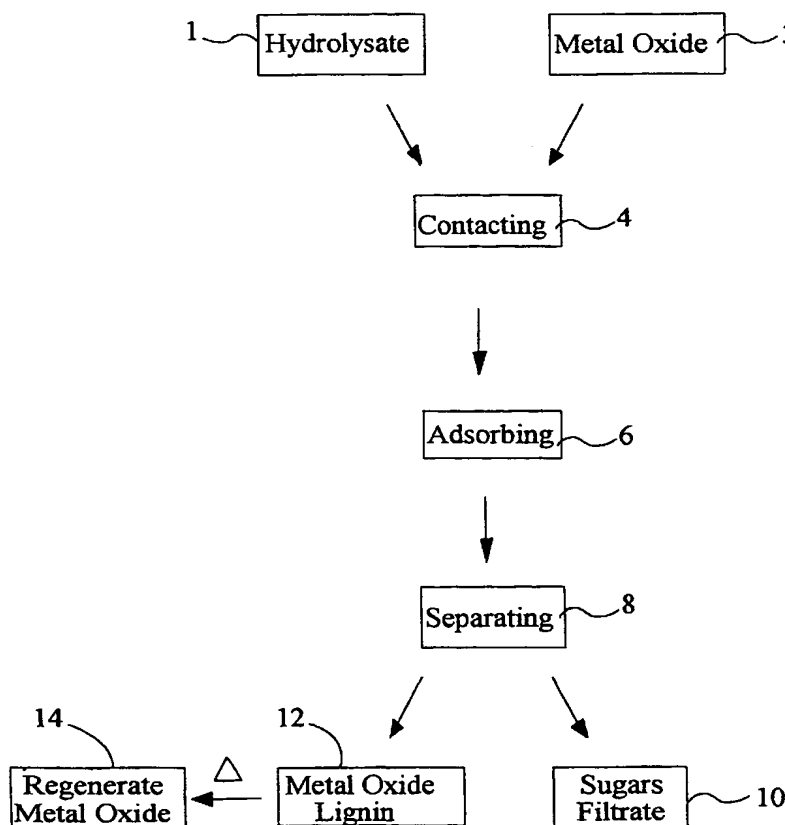
(74) Agent: WHITE, Paul, J.; National Renewable Energy  
Laboratory, 1617 Cole Boulevard, Golden, CO 80401 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
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HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK,  
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(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: PHENOL REMOVAL PRETREATMENT PROCESS



(57) Abstract: A process for removing phenols from an aqueous solution is provided, which comprises the steps of contacting a mixture comprising the solution and a metal oxide, forming a phenol metal oxide complex, and removing the complex from the mixture.

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**Published:**

— *without international search report and to be republished upon receipt of that report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



## **Phenol Removal Pretreatment Process**

### **Contractual Origin of the Invention:**

The United States Government has rights in this invention pursuant to Contract No.  
5 DE-AC36-99GO10337 between the United States Department of Energy and the Midwest  
Research Institute.

### **Technical Field:**

The present invention relates to phenol removal and, in particular to a process of  
removing phenols from an aqueous solution, such as a biomass-hydrolyzate medium.

### **Background Art:**

The efficiency of methods for the selective removal of biomass-derived-phenolic-  
compounds, from an aqueous feedstock is a limiting step in any microbial process for the  
conversion of biomass dissolved sugars into fuels or chemicals. It is also desirable in some  
applications to remove these aromatic compounds because they contaminate fresh water  
15 streams after a forest fire, and process water used in the production or recycling of pulp and  
paper.

A distinct disadvantage of the prior art methods has heretofore been the inefficiency  
and low selectivity of the separation process when applied to an aqueous hydrolyzate. One  
prior method solution involves an extraction of the aqueous hydrolyzate using a series of  
20 organic solvents, such as ethyl acetate, THF or methyl isobutyl ketone. However, in an organic  
solvent extraction, the water soluble biomass-derived-phenolic compounds remain in the  
aqueous phase with the dissolved sugars. Another method comprises filtration of the aqueous  
hydrolyzate through an activated carbon filter. However, with this method, a disadvantage is  
that the activated carbon removes, in addition to the phenol component, many other organic  
25 compounds resulting in an inefficient process.

### **Disclosure of the Invention:**

Therefore, it is an object of the invention to provide a process for removing phenols  
from an aqueous solution.



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It is a further object of the invention to provide a process for the removal of phenols from dissolved sugars in an aqueous biomass-hydrolyzate medium.

It is a yet another object of the invention to provide a biomass pretreatment process for removing lignin-derived phenolic compounds from dissolved sugars in an aqueous biomass  
5 hydrolyzate medium, the process of which is capable of regeneration.

The foregoing specific objects and advantages of the invention are illustrative of those, which can be achieved by the present invention and are not intended to be exhaustive or limiting of the possible advantages which can be realized. Thus, those and other objects and advantages of the invention will be apparent from the description herein or can be learned from  
10 practicing the invention, both as embodied herein or as modified in view of any variations which may be apparent to those skilled in the art.

To overcome the problems of the prior art methods and in accordance with the purpose of the invention, as embodied and broadly described herein, a process for removing phenols from an aqueous solution is provided which comprises the steps of contacting a mixture  
15 comprising the solution and a metal oxide, forming a phenol metal oxide complex, and removing the complex from the mixture.

#### **Brief Description of the Drawings:**

The accompanying drawing, which is incorporated in and which constitutes a part of the specification, illustrates at least one embodiment of the invention and, together with the  
20 description, explains the principles of the invention.

Figure 1 is a flow chart of an embodiment of the process.

#### **Description of the Preferred Embodiments:**

Unless specifically defined otherwise, all technical or scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this  
25 invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are now described.

As used herein the term Aphenolic@ is an adjective meaning a member of the class of phenols. APhenols@ means the class of aromatic compounds in which one or more hydroxyl





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groups are attached directly to a benzene ring. Examples of phenols include phenol, cresol and resorcinol. ABiomass-derived phenols@ include the compounds known as guaiacol, syringol, isoeugenol and vanillin.

5 The process uses a metal oxide, such as titanium dioxide, for the selective adsorption and removal of phenolic compounds from an aqueous solution, such as a biomass-hydrolyzate medium. Dissolved sugars in the solution are thereby concentrated. Adsorption is highly selective, and provides an efficient method for the fractionation of a biomass-hydrolyzate, 90% of the hydrolyzate=s dissolved lignin being removed without a measurable decrease in the solution=s dissolved sugar concentration. Selectivity is attributable to the metal oxide=s  
10 preferential binding with those oxygen molecules which are located on adjacent (ortho) carbons of the aromatic ring structures.

With reference now to Figure 1, the starting material is a biomass hydrolysis liquor 1. The hydrolysis liquor 1 is mixed in contacting step 4, as a suspension, with a metal oxide 2, such as a Norton Chemical Process Products Corporation, Akron, Ohio high-surface-area TiO<sub>2</sub>  
15 1/8 " extrudate type XT25384. High separation efficiency is generally achieved by using an amount or weight (wt) of TiO<sub>2</sub>, which is twice the estimated phenol content of the liquor. This ratio varies, however, with the form, source, active surface area, and liquid-contact surface area of the TiO<sub>2</sub>, to be used. Separation efficiency also varies with the age of the aqueous mixture and source of the biomass. Producing hydrolyzate under conditions of high severity also  
20 reduces the separation efficiency.

Selective adsorpting step 6 is accomplished using all grades of TiO<sub>2</sub>. The rate and efficiency of the adsorption of aromatic compounds with TiO<sub>2</sub> is dependent upon the TiO<sub>2</sub> active surface area. Anatase titanium dioxide, preferable to the rutile form, may be of any high-surface-area formulation, including powders, thin-films, sol-gel crystals, and extruded  
25 pellets. Vanadium oxide and zirconium oxide, and at pH in a range of greater than 7.0 manganese dioxide, silica, and alumina, may also be used.

Depending upon the quantity of the aromatic compounds to be removed, a batch reaction vessel or plug flow reactor may be used as an adsorption vessel. In a batch reactor, the retention time is preferably 30 minutes. In a plug flow column, the retention time is



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preferably 15 minutes. These retention times typically result in a separation of up to 90-weight % of the aromatics from the hydrolyzate 1. Longer retention times are desirable where the separation is carried out at a low pH. For example, the adsorption is slower in the pH range of 2 - 6 and occurs more rapidly when the pH is in the range of 7 -10.

5           The process retains its efficiency and selectivity throughout a temperature in the range of 20°C-90°C. Performing the selective adsorption under conditions of elevated temperature and pH does not affect adsorption selectivity relative to the carbohydrate fraction.

          However, above pH 6, some carbohydrate degradation products, such as 5-(hydroxymethyl) furfural and furfural, are also adsorbed on the metal oxide surface. At  
10 combinations of higher pH and temperature some entrainment of soluble salts occurs on the metal oxide surface when the hydrolyzate 1 and metal oxide 2 mixture contains salts having a lower solubility at higher temperatures, such as calcium sulfate. Raising both the temperature and the pH does not affect the adsorption selectivity of this process for lignin.  
After contacting the hydrolyzate and metal oxide, adsorption preferably includes agitating the  
15 mixture for a time sufficient to allow the colloidal particles to deposit on the TiO<sub>2</sub> particulate surfaces, as indicated by a clearing of the suspension, and allowing the suspension to settle at room temperature for 1 hour. The adsorbed complex is then separated in separation step 8. Separation may be accomplished using a glass-fiber filter. The carbohydrate fraction of the hydrolysis liquor is contained in the sugars filtrate 10.

20           A unique aspect of the invention is its high separation selectivity for lignin in an aqueous hydrolysis liquor having an excess of monomer sugars. More than 90% of the solubilized lignin can be removed from the hydrolyzate without any loss of glucose or xylose. When using TiO<sub>2</sub> extruded pellets as an adsorbent, a slight concentration effect is observed during the adsorption process. This effect may be due to hydration of the metal oxide and the  
25 exclusion of sugars from the metal oxide's surface. Solid state nuclear magnetic resonance analysis of lignin model compounds, adsorbed on the TiO<sub>2</sub> surface, has suggested that the lignin selectivity is due, at least in part, to an affinity of titanium for adjacent oxygen molecules which are located on the aromatic ring structure of the adsorbed substrates. It has been found that, through chemical shifts in <sup>13</sup>C nmr between lignin model compounds both before and after

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complexation with titanium alkoxides, these molecules bind preferentially through the phenolic oxygen and the oxygen of the adjacent methoxyl group. The biomass-derived aromatic substituents have two main substitution patterns, commonly known as guaiacyl and syringyl, which contain the functional groups necessary for the selective fractionation. Although  
5 titanium, and many other transition metals, are known to be highly oxyphilic, the affinity of this functionality for these metal oxides is so strong that in the presence of these aromatic compounds, even highly oxygenated carbohydrate-derived compounds are excluded from the metal oxide surface.

The process may also include a regeneration step 14. In this step, the  $\text{TiO}_2$  adsorbents  
10 are easily regenerated using combustion of the complex at  $400^\circ\text{C}$  for 15 minutes. An estimated 100-500 regeneration cycles may be utilized without a significant reduction in adsorption capacity or selectivity. It is preferred to regenerate the  $\text{TiO}_2$  at a temperature of less than  $600^\circ\text{C}$  in order to avoid an anatase to rutile form conversion, which decreases the metal  
oxide's capacity for adsorption. A simple regeneration wash step using dilute sulfuric acid  
15 may also be used to increase the lifetime of  $\text{TiO}_2$  adsorbents when the contacting step 4 is carried out at a high pH. When using a pH greater than 7, an additional step of acid washing the adsorbent is desirable. Regeneration of a manganese dioxide adsorbent has also been demonstrated at  $575^\circ\text{C}$  for 15 minutes.

#### EXAMPLE

20 This example illustrates the process of removing phenolic compounds from an aqueous biomass hydrolysis liquor using  $\text{TiO}_2$  as the metal oxide. The hydrolysis liquor was an acid hydrolyzate of hybrid yellow poplar. In this example the following three samples were prepared. Sample No. 1 was prepared by mixing a 50 ml aliquot, of a well mixed hydrolysis liquor containing a larger amount of suspended solids, in contact with 10 grams of Norton  
25 high-surface-area  $\text{TiO}_2$ , in a 100 ml beaker. The sample was agitated by hand for approximately 5 minutes, until the mixture became clear (colloidal particulates deposited on the surface of the  $\text{TiO}_2$ ). The mixture was allowed to settle at room temperature for 1 hour. The  $\text{TiO}_2$  mixture was filtered through a glass Watman GFC filter and the filtrate was stored in a glass container.

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Samples Nos. 2 and 3 were prepared by mixing a 50 ml aliquot, of a well-mixed hydrolysis liquor again containing a large amount of suspended solids, in contact with 10 grams of high surface area  $\text{TiO}_2$  in a 100 ml beaker. Unlike sample No. 1, the  $\text{TiO}_2$  in sample No. 2 was left in solution without stirring at room temperature for 8 hours (sample No. 2) prior to the removal of the  $\text{TiO}_2$  phenolic-adsorption-complex, by gravity filtration. Half of the liquid (20 ml) was decanted and filtered for analysis, and the other half of the solution was retained in contact with the  $\text{TiO}_2$  overnight (sample No. 3). The beaker was covered with aluminum foil to minimize evaporation. After 20 hours, the remaining liquid of sample No. 3, was decanted from the  $\text{TiO}_2$  complex and filtered through a Watman GFC glass filter. The filtrates for each sample were diluted in dilute  $\text{H}_2\text{SO}_4$  and analyzed for their phenol concentrations by measuring UV absorbency at 204 nm. In addition, the glucose concentration of the filtrate was measured for each sample using a Yellow Springs Instruments glucose analyzer.

The results of this example are summarized in Table 1. In the table, most of the adsorption occurs within the first hour and very little change is observed in either adsorption or selectivity with prolonged exposure. The absorbance at 204 nm (measured using a ultra-violet/visible spectrometer) reflects the concentration of the phenolic compounds remaining in the treated liquor. The absorbance at 282 nm reflects the concentration of furfural and 5-(hydroxymethyl) furfural. The dilution factor (D) was the dilution used to bring the solution to a concentration where the absorbency is proportional to the concentration.

TABLE 1

Sample	Absorbance 204 nm	Absorbance 282 nm	D	Lignin mg/ml	Glucose mg/ml
Original Liquor	1.0763	0.591308	641	6.3	9.4
Sample No. 1 (1 h)	2.14941	0.409973	51	1	10.8
Sample No. 2 (8 h)	1.48932	0.448135	51	0.7	11
Sample No. 3 (16 h)	1.29463	0.5885	51	0.6	10.3

While the present invention has been illustrated and described with reference to particular structures and methods, it will be apparent that other changes and modifications can be made therein with the scope of the present invention as defined by the appended claims.

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Claims

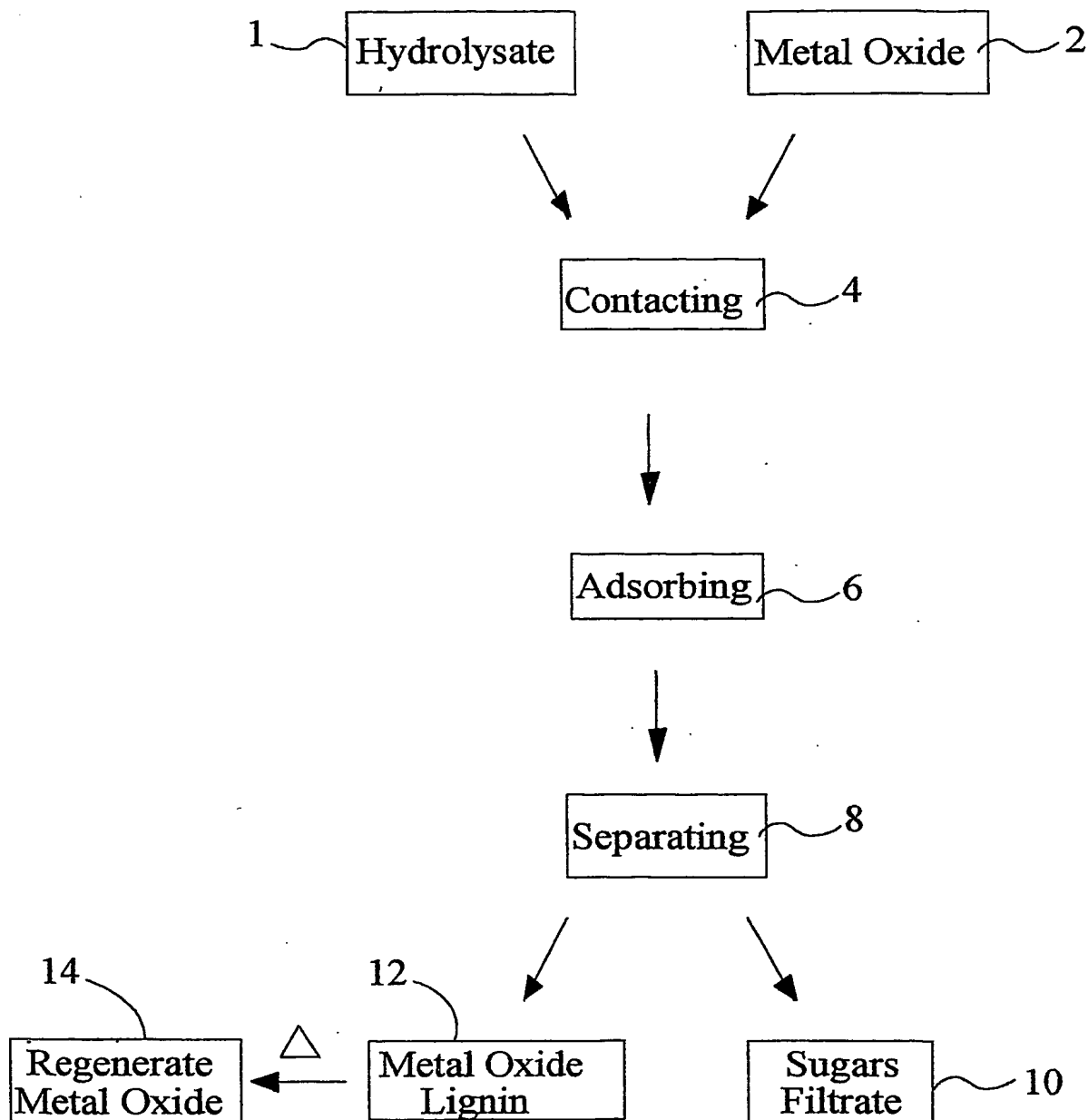
1. A process for removing phenols from an aqueous solution comprising the steps of:
  - (a) contacting a mixture comprising the solution and a metal oxide;
  - 5 (b) forming a phenol compound metal oxide complex; and
  - (c) removing the phenol metal oxide complex from the mixture.
2. The process of claim 1 wherein the metal oxide is selected from the group consisting of titanium dioxide, vanadium oxide, and zirconium oxide.
3. The process of claim 1 wherein the phenolic compound is lignin or biomass-derived.
- 10 4. The process of claim 1 further comprising adjusting the mixture to a pH greater than 7.0 after contacting.
5. The process of claim 1 wherein the metal oxide is selected from the group consisting of manganese dioxide, silicon dioxide, and aluminum oxide, and further comprising adjusting the mixture to a pH in the range of 1.5-11 after contacting.
- 15 6. The process of claim 1 further comprising regenerating the metal oxide after removing the phenol metal oxide complex from the mixture.
7. The process of claim 1 wherein the solution is a biomass hydrolyzate and the phenols are biomass-derived.
8. The process of claim 6 wherein regenerating comprises heating in the presence of  
20 oxygen.

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*FIG. 1*



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(71) Applicant (*for all designated States except US*): **MID-WEST RESEARCH INSTITUTE** [US/US]: 425 Volker Boulevard, Kansas City, MO 64110 (US).

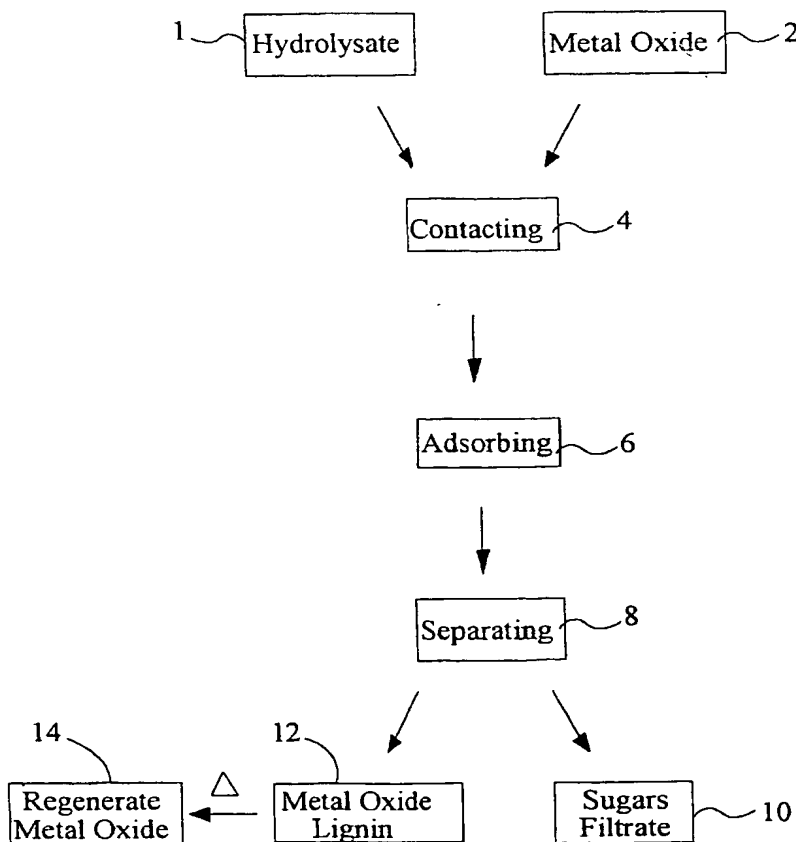
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,

(72) Inventor; and

(75) Inventor/Applicant (*for US only*): **HAMES, Bonnie, R.**

[Continued on next page]

(54) Title: PHENOL REMOVAL PRETREATMENT PROCESS



(57) Abstract: A process for removing phenols from an aqueous solution is provided, which comprises the steps of contacting a mixture comprising the solution and a metal oxide, forming a phenol metal oxide complex, and removing the complex from the mixture.

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IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(88) Date of publication of the international search report:  
21 February 2002

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*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*





## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/11806

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C02F1/68 C02F1/58

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 4 595 489 A (SCOUTEN CHARLES G) 17 June 1986 (1986-06-17) the whole document ---	1,2,6 3-5,7,8
X A	EP 0 112 723 A (EXXON RESEARCH ENGINEERING CO) 4 July 1984 (1984-07-04) the whole document -----	1,6 2

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

1 November 2001

Date of mailing of the international search report

08/11/2001

Name and mailing address of the ISA

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Authorized officer

Serra, R



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/11806

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4595489	A	17-06-1986	BR 8307122 A	07-08-1984
			EP 0112723 A2	04-07-1984
			JP 59130230 A	26-07-1984
			US 4661637 A	28-04-1987
			ZA 8309596 A	28-08-1985
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EP 0112723	A	04-07-1984	BR 8307122 A	07-08-1984
			EP 0112723 A2	04-07-1984
			JP 59130230 A	26-07-1984
			US 4595489 A	17-06-1986
			US 4661637 A	28-04-1987
			ZA 8309596 A	28-08-1985
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# PATENT COOPERATION TREATY

## PCT

### INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 31 DEC 2002

Applicant's or agent's file reference PCT/98-21	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US01/11806	International filing date (day/month/year) 10 April 2001 (10.04.2001)	Priority date (day/month/year) 10 April 2000 (10.04.2000)
International Patent Classification (IPC) or national classification and IPC IPC(7): C02F 1/68, 1/58 and US Cl.: 208/263		
Applicant MIDWEST RESEARCH INSTITUTE		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 3 sheets, including this cover sheet.  
☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 0 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 02 November 2001 (02.11.2001)	Date of completion of this report 22 October 2002 (22.10.2002)
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks. Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Chester T. Barry Telephone No. 703-308-0651

Form PCT/IPEA/409 (cover sheet)(July 1998)

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US01/11806

## I. Basis of the report

### 1. With regard to the elements of the international application:\*

- ☒ the international application as originally filed.
- ☒ the description:  
 pages 1-6 \_\_\_\_\_ as originally filed  
 pages NONE \_\_\_\_\_, filed with the demand  
 pages NONE \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
- ☒ the claims:  
 pages 7 \_\_\_\_\_, as originally filed  
 pages NONE \_\_\_\_\_, as amended (together with any statement) under Article 19  
 pages NONE \_\_\_\_\_, filed with the demand  
 pages NONE \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
- ☒ the drawings:  
 pages 1 \_\_\_\_\_, as originally filed  
 pages NONE \_\_\_\_\_, filed with the demand  
 pages NONE \_\_\_\_\_, filed with the letter of \_\_\_\_\_.
- ☐ the sequence listing part of the description:  
 pages NONE \_\_\_\_\_, as originally filed  
 pages NONE \_\_\_\_\_, filed with the demand  
 pages NONE \_\_\_\_\_, filed with the letter of \_\_\_\_\_.

### 2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

### 3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in printed form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

### 4. ☐ The amendments have resulted in the cancellation of:

- ☐ the description, pages NONE
- ☐ the claims, Nos. NONE
- ☐ the drawings, sheets/fig NONE

### 5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.  
PCT/US01/11806

## V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. STATEMENT

Novelty (N)	Claims <u>2, 4, 5</u>	YES
	Claims <u>1, 3, 6 - 8</u>	NO
Inventive Step (IS)	Claims <u>2, 4, 5</u>	YES
	Claims <u>1, 3, 6-8</u>	NO
Industrial Applicability (IA)	Claims <u>1-8</u>	YES
	Claims <u>NONE</u>	NO

### 2. CITATIONS AND EXPLANATIONS

Claims 1, 3, 6, 7, 8 lack novelty under PCT Article 33(2) as being anticipated by USP 4 595 489 to SCOUTEN. SCOUTEN describes a process for removing bio-mass derived, i.e., coal-derived, phenols from aqueous solution comprising contacting the solution with metal hydroxide, forming phenol metal oxide complexes, e.g., metal phenate, and removing the phenol metal complex from solution. See Abstract and col 1 line 19, and claims 1-11. Afterwards, the phenol is recovered by steam stripping in the presence of air (including oxygen). See col. 10 lines 5 - 13.

